Journal of Luminescence 193 (2018) 51–60

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effect of the heat treatment on the spectroscopic properties of Er^{3+}-Yb^{3+}-doped transparent oxyfluoride nano-glass-ceramics

G. Gorni[a], R. Balda[b,c,*], J. Fernández[b,c], L. Pascual[d], A. Durán[a], M.J. Pascual[a]

[a] Instituto de Cerámica y Vidrio ICV-CSIC, Madrid, Spain
[b] Departamento de Física Aplicada I, Escuela Superior de Ingeniería, Universidad del País Vasco UPV/EHU, Bilbao, Spain
[c] Centro de Física de Materiales UPV/EHU-CSIC, San Sebastian, Spain
[d] Instituto de Catálisis y Petroleoquímica ICP-CSIC, Madrid, Spain

ARTICLE INFO

Keywords:
Glass ceramics
Oxyfluoride
Er^{3+}/Yb^{3+} co-doping
Energy transfer
Upconversion

ABSTRACT

Er^{3+}-doped and Er^{3+}-Yb^{3+}-co-doped transparent oxyfluoride glass-ceramics (GCs) containing LaF_3 nano-crystals (NCs) have been prepared by the melting-quenching method and adequate thermal treatments. A detailed structural characterization, performed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM), confirms the precipitation of LaF_3 NCs with a size in the 10–15 nm range. The crystal growth is fast in the very beginning, from a few min up to 3–5 h of treatment at 620 °C and then it slows down, up to 20 h. A SiO_2 enriched viscous barrier is formed around the NCs, thus preventing further crystal growth. The incorporation of Er^{3+} and Yb^{3+} ions into the NCs is proved by HR-TEM and energy dispersive X-ray spectroscopy (EDXS) analysis. Photoluminescence measurements have been performed upon visible and near infrared excitation. The energy transfer between Yb^{3+} and Er^{3+} ions is evidenced by the enhancement of the near infrared and Up-Conversion (UC) emissions of Er^{3+} ions in the co-doped samples under 980 nm excitation. A moderate back transfer from Er^{3+} to Yb^{3+} ions has been also observed under near infrared excitation of Er^{3+} ions at 800 nm. Upconverted green (($^2H_{11/2}$,$^4S_{3/2}$) → $^4I_{15/2}$) and red ($^4F_{9/2}$ → $^4I_{15/2}$) emissions were observed in all samples and attributed to a two photon process. The strong enhancement of the UC emission for the co-doped glass-ceramics samples further confirms the incorporation of the rare-earth ions in the LaF_3 NCs with a lower maximum phonon energy environment which reduces multi-phonon relaxation rates. Different red-to-green emission ratios are obtained depending on the heat treatment conditions for the glass-ceramic samples.

1. Introduction

Glass-ceramics have become increasingly important in the last decades because they combine the advantages of glass processing with the good properties of ceramic (or crystalline) materials, such as good mechanical, thermal and optical properties. Paying attention to optical materials for Vis-NIR application, transparent glass-ceramics are very attractive because they allow obtaining an active crystal phase in a glass matrix. In particular, oxide matrices in which low phonon energy (200–500 cm^{-1}) fluoride crystals precipitate, commonly known as oxyfluoride glass-ceramics (GCs), have been extensively studied [1–5]. From the pioneering work of Wang and Ohwaki in 1993 [6], concerning the efficient green and red Upconversion (UC) emission in Er^{3+}-Yb^{3+} co-doped GCs containing $Pb_xCd_{1-x}F_2$ nano-crystals (NCs), many different fluoride crystal phases have been studied, showing the possibility of effectively improving the luminescence of rare-earth ions (REI) when they are embedded in fluoride NCs.

REI in their most stable oxidation state (3+) show a wide range of intra-band transitions (4f-4f), from UV to NIR, that are weakly affected by the ligand field due to the s an p orbital shielding, as compared for example to noble metals [7,8]. Their emission bands are roughly centred at the same energy in different host materials, glasses or crystals. This property converts them in the most important active ions for technological applications in the Vis-NIR range. Therefore, the continuous research for more efficient REI host materials has become the crucial point for the development of the new generation of optical materials. Even more interesting is the possibility of combining different REI to produce Down-Conversion (DC) and UC processes in which photons of smaller or higher energies are emitted upon absorption of incident photons [9]. Known examples are the DC processes in the Pr^{3+}-Yb^{3+} doped materials [10–15] with applications in solar cells for blue to NIR light conversion, or the UC processes for Er^{3+} and Er^{3+}-Yb^{3+} ions with bio applications [16–24], where NIR light is used to analyse organic tissues, thanks to its deep penetration, and then

* Corresponding author at: Departamento de Física Aplicada I, Escuela Superior de Ingeniería, Universidad del País Vasco UPV/EHU, Bilbao, Spain.
E-mail address: rolindes.balda@ehu.eus (R. Balda).

http://dx.doi.org/10.1016/j.jlumin.2017.05.063
Received 26 April 2017; Received in revised form 19 May 2017; Accepted 23 May 2017
Available online 24 May 2017

converted into visible light. Further applications of UC materials can be found in the field of optical amplification and lasers [25–28].

Among different fluoride crystal phases, those containing REI such as Gd^{3+} and La^{3+} that show neither Vis nor NIR emission bands [29–31], offer the possibility of easily exchanging the REI of the host by those used as dopants due to their similar size and electronic configuration.

In a previous work performed by our group [32], describing Nd^{3+} doped LaF_3 GCs, the Nd^{3+} migration to the fluoride crystals was showed; using a selective excitation it was possible to select Nd^{3+} ions embedded in the LaF_3 crystals, this leading to a highly improved luminescence efficiency and similar emission spectra to those obtained for pure Nd^{3+} doped LaF_3 crystals. In this paper, both structural and optical results of bulk glasses and GCs containing LaF_3 crystals doped with Er^{3+} and co-doped with Yb^{3+} for NIR and UC emission are presented. There is abundant literature regarding Er^{3+} and Er^{3+}-Yb^{3+} doped LaF_3 materials, nevertheless, most of them refer to powders or nanoparticles dispersed in liquid phase [24,33–39] and only a very few are related to bulk or bulk-derived GCs [40–42]. The development of inorganic bulk materials with excellent luminescence properties and high ability to transmit light is useful for many optoelectronics applications such as solid state lasers, optical amplifiers, and sensors among others.

2. Experimental

2.1. Materials preparation

Glasses of composition $55SiO_2$-$20Al_2O_3$-$15Na_2O$-$10LaF_3$ (55Si-10La) doped with $0.5Er^{3+}$, $0.5Er^{3+}$-$2Yb^{3+}$ and $0.5Er^{3+}$-$4Yb^{3+}$ (mol %) have been prepared by the melting-quenching technique using as raw materials: SiO_2 (Saint-Gobin 99.6%), Al_2O_3 (Panreac), Na_2CO_3 (Sigma Aldrich, > 99.5%), LaF_3 (Alfa Aesar, 99.9%), ErF_3 (Alfa Aesar, 99.99%) and YbF_3 (Alfa Aesar, 99.99%). The batches were calcined at 1200 °C for 2 h, melted at 1650 °C for 1.5 h and then quenched onto a brass mould. The batches were melted again for 30 min and then quenched onto a cold brass mould to improve glass homogeneity. An annealing process at 600 °C for 30 min was performed on the as made glasses to eliminate residual stresses. In the following, glass samples will be labelled by G0.5, G0.5-2, G0.5-4 for Er^{3+} and Yb^{3+} concentrations equal to 0.5, 0.5-2 and 0.5-4, respectively, while corresponding glass-ceramics will be denoted with GC0.5, GC0.5-2 and GC0.5-4. Glass-ceramics samples have been obtained upon heat treatments of glass pieces at 620 °C-from 5 min up to 80 h and at 660 °C-20 h, using a heating rate of 10 °C/min in all cases. Glass sheets (1 cm × 1 cm × 2 mm) were treated at 620 °C-20 h and 40 h and at 660 °C-20 h and then polished for optical characterization. One glass sheet of each composition was polished but not heat treated. In this way it was possible to compare the as made glasses with the corresponding GCs, allowing to evaluate the influence of the treatment time/temperature (for a fixed temperature/time) onto the optical properties.

The density of samples was measured by the Archimedes's method using distilled water as liquid.

2.2. Thermal and dilatometric characterization

Small glass specimens (15 mm × 5 mm × 5 mm) were cut and analysed by dilatometry (Netzsch DIL 402 PC) using a heating rate of 5 °C/min. By a linear fit of the curve in the range 100–450 °C the dilatometric expansion coefficient α was obtained. The glass transition temperature (T_g) and the dilatometric softening point (T_d) were also obtained. Differential thermal analysis (SDT Q600 – TA Instruments) was performed on bulk specimens in the range 25–1000 °C using 20–30 mg of glass with particle size in the range 1–1.25 mm. DTA curves were obtained with heating rates of 10 °C/min.

2.3. Structural characterization

Bulk glass specimens were treated in the range 620–660 °C from 5 min up to 80 h to convert them into GC samples and then milled and sieved to a particle size lower than 60 μm and analysed by XRD (Bruker D8 Advance) in the range 10–70° with a step size of 0.02°. Peak fit was performed using the Pseudo-Voigt function and the crystal size was estimated using the Scherrer's equation:

$$D = \frac{0.94\lambda}{\cos\theta\sqrt{B_m^2 - B_i^2}} \quad (1)$$

where λ is the wavelength (1.54056 Å – CuKα$_1$), B_m the full width half maximum of the LaF_3 peak (111) and θ its diffraction angle. The constant factor 0.94 is assumed considering spherical crystals. The instrumental broadening B_i has been also taken into account.

High resolution transmission electron microscopy (HRTEM) data as well as scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) images and X-ray energy dispersive spectra (EDXS) were recorded on a JEOL TEM/STEM 2100F field emission gun transmission electron microscope operating at 200 kV and equipped with an EDXS spectrometer Oxford INCA X-sight system. XEDS analysis was performed in STEM mode. Small amounts of powders were dissolved in ethanol and then a drop was deposited onto a copper grid supporting a lacey carbon film.

2.4. Optical characterization

UV–Vis absorption spectra were collected in the range 300–1700 nm using a double beam spectrophotometer (Perkin Elmer LAMBA 950).

The steady-state emission measurements were made with a Ti-sapphire ring laser (0.4 cm^{-1} linewidth) and an Argon laser as exciting light. The fluorescence was analysed with a 0.25 monochromator, and the signal was detected by an extended IR Hamamatsu H10330A-75 photomultiplier and finally amplified by a standard lock-in technique. Visible emission was detected by a Hamamatsu R636 photomultiplier. Lifetime measurements were obtained by exciting the samples with a Ti-sapphire laser pumped by a pulsed frequency doubled Nd:YAG laser (9 ns pulse width), and detecting the emission with Hamamatsu H10330A-75 photomultiplier. Data were processed by a Tektronix oscilloscope. All measurements were performed at room temperature.

3. Results and discussion

3.1. Glasses and GCs

Glasses and GCs perfectly transparent of all the compositions were successfully obtained after the thermal treatments. A little bluish color is observed for 0.5–4 glass and GC samples, related to light scattering produced by phase separation and crystallization due to higher dopants concentration. Anyway good transparency is still maintained, as shown in Section 3.4.1, with a slight increase in the absorption edge around 400 nm.

3.2. Thermal and dilatometric characterization

Dilatometric measurements showed that Er^{3+} doped glass has T_g around 596 °C (598 °C for the un-doped glass) while in co-doped samples T_g diminishes down to 587 °C. This behaviour is likely associated to a higher fluorine content in the co-doped samples, this decreasing T_g. The dilatometric softening point T_d diminishes from 670 °C to 656 °C when increasing Yb^{3+} content, but the dilatometric expansion coefficient α is around 9.2 × 10^{-6} m^{-1} for all the glasses, practically independent of Yb^{3+} content. The transition and crystallization temperatures were determined by DTA analysis. The crystal-